COLOUR REMOVAL OF THREE REACTIVE DYES BY UV LIGHT EXPOSURE AFTER ELECTROCHEMICAL TREATMENT

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Abstract

This study applies UV light irradiation after a low current density electrochemical treatment to degrade reactive dyes to remove wastewater colour. The combination of these two techniques improves the quality of the treated effluent with respect to only an electrochemical treatment. Synthetic dyeing effluents containing a reactive dye (C.I. Reactive Orange 4, C.I. Reactive Black 5 or Procion Navy H-EXL) and Na_2SO_4 were studied. Ti/Pt oxides electrodes and UV irradiation lamp (6 W, 254 nm maximum emission) were used. Kinetic constants of the UV irradiation step were calculated. The influence of chloride ion at 3 and 6 mA/cm^2 was evaluated. Results showed that, with a very small Cl^- concentration (in the order of the net water content) the combined techniques provided full decolourization. The possible presence of 25 organic halogenated compounds was studied by Gas Chromatography-Mass Spectrophotometry (GCMS). Only four of them were detected after the electrochemical treatment at low intensity, mainly chloroform. Its concentration was found to be highly dependent of the Cl^- concentration, being much lower when reducing the amount of chloride ion. In all cases, the chloroform concentration was dramatically reduced by further UV irradiation which destroyed it up to a 75%.

Keywords: reactive dye, decolourization, UV light, textile wastewater, dyeing bath, GCMS.

1. Introduction

Worldwide increasing demand of new fabrics increases the consumption of dyes that is estimated in 800,000 t annually [1]. Reactive dyes represent an important fraction of the commercialized synthetic dyes used (approximately 12% of the worldwide production) [2]. The main environmental problem associated with the reactive dyes is their low exhaustion. Frequently, the fixation efficiency of these dyes range between 60% and 90% [3] consequently substantial amounts of unfixed dyes are released in the wastewater.

Several technologies to remove colour of wastewater have been studied and some of them are applied nowadays. These technologies can be classified in four main groups. *Oxidation techniques*: electrochemical oxidation, peroxides, ozone, etc. *Physicochemical techniques*: adsorption, ion exchange, coagulation/flocculation. *Membranes*: nanofiltration, reverse osmosis, etc, and *Biologic techniques*: enzymatic decolourization processes. Sometimes the combined use of two techniques provides better results and it is more and more frequent. This work focuses in a combined process based on UV light exposure after an electrochemical treatment.

Electrochemical processes are electronic transferences between two compounds where these transferences take place between the substratum and the metallic electrodes, usually inert, by means of the electrical current [4]. Generally, these techniques work under soft conditions (room temperature and atmospheric pressure) but their main advantage is that they do not need the addition of any chemical reagent [5].

Some authors have applied the electrochemical techniques to the destruction of toxic or non biodegradable organic compounds in wastewater (phenols, cyanides, PCB's…). In the case of textile organic dyes, the electrochemical treatment has been mainly proposed for the colour removal [6] although the mineralization of residual dyes has also been reported [7]. From a practical point of view, the electrochemical treatment is only useful to remove effluents color, discarding the complete mineralization to CO_2 and H_2O because of its high cost [8].

Reactive dyes are usually difficult to biodegrade [9] but if they undergo an electrochemical treatment, they can be broken into colourless smaller molecules which can be removed in a further biological treatment. Most of dyes contain azo groups (-N=N-) that can be oxidized to nitrocompounds when oxidation occurs or reduced to amines when reduction occurs [10]. Although some reduction electrochemical treatments of colour removal of textile effluents have been reported [11], the oxidation treatments are more common.

Oxidation processes can be classified in two types: those which take place on the electrode surface, known as *direct oxidation* and those which take place due to the action of molecules formed in the anode, known as *indirect oxidation*. Both processes can occur either in the same reactor or in a different one [12] and simultaneously or not [13]. The most common species in indirect oxidation are: hydroxyl radical ($OH^{\bullet}$), chlorine and hypochlorite in water purifying, ozone in sterilization and oxidation of organic matter, and redox pairs species such as Cr(VI)/Cr(III).

Many authors establish that $OH^{\bullet}$ is the most appropriate to degrade effluents when using indirect oxidation [14, 15]. Alternatives such as HCl for the degradation of organic compounds in textile effluents have been proposed by others [16].

One of main inconvenients of electrochemical treatments is their high energy cost which can be reduced by using indirect electrochemical treatments in the presence of Cl^-. In this case the formation of haloforms or other halogenated compounds is observed when the chloride oxidation products react with organic matter. The haloforms concentration was dependent on the current density applied during the electrochemical treatment [10]. For this reason, in this work we propose its combined use with UV exposure. Combination of both techniques allows the decolourization of residual dyes at a lower current density which implies a lower cost. Electrochemical treatment is used only to initiate the degradation of the dyes. In this first step, different radical species are formed, able to react with organic compounds by an indirect oxidation reaction which is further catalysed by applying UV light. Simultaneously, this UV treatment achieves the decomposition of the small amount of halogenated compounds generated during the electrochemical treatment.

UV radiation alone is not capable to destroy reactive dyes as they are resistant to direct UV light exposure [17]. Some authors have reported the use of UV light exposure with electrochemical treatment as a proper way to reduce COD, BOD_5 and NH_3 content in wastewater [18]. Other authors have applied UV light using TiO_2 as a photocatalizer to

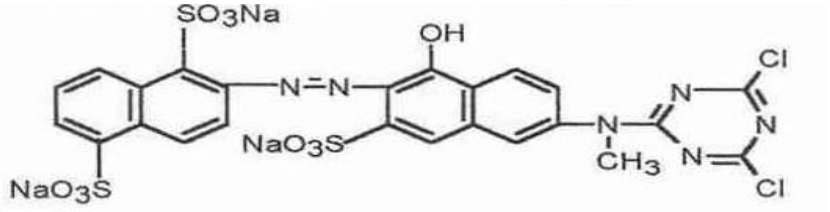
degrade dyes [19]. Although colour removal by electrochemical treatment followed by UV exposure has already been reported [7], studies about their combined use are still very scarce and some aspects must be clarified before the application of this process at an industrial level.

The two main goals of this study are the optimization of the electrochemical and further UV light irradiation whole treatment to achieve good colour removal of simulated textile effluents at a low cost and to find the conditions in which halogenated compounds content is minimized.

2. Materials and methods

In this work three reactive dyes, kindly provided by DyStar, were selected: Procion Orange MX-2R (Colour Index Reactive Orange 4), reactive group dichlorotriazine and chromophore azo; Remazol Black B 133 (Colour Index Reactive Black 5), double reactive group sulfatoethylsulfone and chromophore diazo; Procion Navy H-EXL, with a double monochlorotriazine reactive group and chromophore azo. From this section, these dyes will be referred in the text as: RO4, RB5 and PN H-EXL respectively. Figure 1.a and 1.b shows the two available structures of the dyes. The formula corresponding to PN H-EXL has not been published.

(a)



(b)

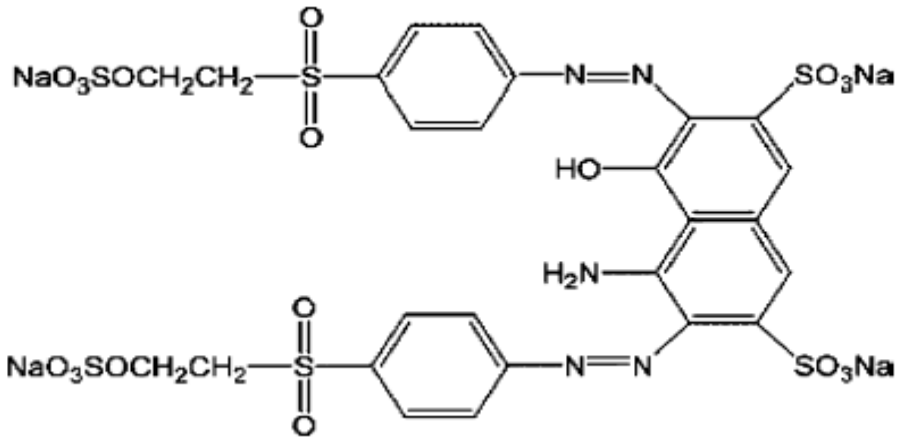


Fig. 1. Chemical structure of (a) C.I. Reactive Orange 4 and (b) C.I. Reactive Black 5

2.1. Reactive dyebath effluent preparation

The dyeing process with reactive dyes is usually carried out at alkaline pH (10-12) with a high concentration of salts (generally NaCl or Na_2SO_4) to accomplish the proper fixation of the dyes. During this step, dyes are linked to the fibre by a chemical reaction. But, simultaneously, there is competitive hydrolysis reaction with the solvent and the hydrolysed dyes (10-40% of the initial amount) must be removed in the wastewater.

Simulated dyebath effluents were prepared in the laboratory in distilled water at 0.1 g L^{-1} of the commercial dyes, previously hydrolyzed to simulate an industrial effluent. The hydrolysis was carried out as follows: the pH was adjusted to 12 with NaOH (Flucka) and then the solution was heated at 80 ºC for two hours. After the hydrolysis, it was let cool down to room temperature and the pH was adjusted to 9 with sulphuric acid (Scharlau).

Different concentrations of NaCl, between 0 and 5 g L^{-1}, were added to the effluent to study the effect of Cl^- in decolourization and halogenated compounds formation. As indicated previously, a high concentration of salts is used in the dyeing process. To simulate the conductivity of an industrial effluent, the required amount of sodium sulphate (Scharlau) was finally added to each solution in order to reach a final conductivity of 35.000 µS cm^{-1}.

2.2. Experimental wastewater treatment plant

The experimental plant consists in two different parts: an electrochemical cell (continuous process) followed by an UV exposure device (batch process).

2.2.1. Electrochemical cell

Electrochemical treatments were performed in an undivided electrolytic cell based on the commercial cell ECO 75 (ELCHEM, Germany), which was initially designed to obtain hypochlorite for disinfection. Cathodes were constituted by titanium and anodes were made of titanium covered by platinum oxides. The total surface area of each electrode was 486 cm^2. The volume of the vessel was 1L. The cell was able to treat up to 25 L h^{-1} which allows its use at industrial scale.

The experimental plant was constituted by the electrochemical cell, the pump to feed the system and the deposit to store the treated wastewater. This plant operated continuously, and the flow rate was fixed at 20 L h^{-1}. The source supply allowed regulating the current among 0 and 25 A. The voltage was variable among 0 and 40 V, depending on the current applied and on the conductivity fixed for the treatment.

A range of synthetic effluents containing different chloride ion concentration, from 0 to 5 g L^{-1} of NaCl, were treated in this plant, each of them at two different current densities (3 and 6 mA/cm^2).

2.2.2. UV Device

After the electrochemical treatment, aliquots of 250 mL of effluents were collected, placed in a recipient 8 cm under the UV lamp and irradiated while stirring. For the irradiation, a 6W fluorescent UV light source with a maximum emission spectrum at 254 nm (Vilber Lourmat) was used.

2.3. Analytical measurements

2.3.1 Decolourization measurements

Decolourization was calculated from the initial concentration and dye concentrations at time t (c_i and c_t respectively) by measuring the absorbance at the visible maximum dye absorption wavelength (488 nm for RO4, 583 nm for RB5 and 606 nm for PN H-EXL). Measurements were carried out on the effluent, just after electrochemical treatment and along the UV treatment. During UV exposure, samples were taken and measured every 5 minutes. Decolourization (D) was reported in %:

$$D\ (\%) = \frac{(c_i - c_t)}{(c_i)} \times 100 \quad (1)$$

Absorbance measurements were carried out with a UV-visible spectrophotometer (Shimadzu UV-2401 PC). Dye absorbance has a linear behaviour versus the concentration in the range between 0.001 and 0.020 g L^{-1} according to the equations:

Abs = 29.413c – 0.002 (R^2 = 0.9999) for RO4 (2)
Abs = 30.858c – 0.002 (R^2 = 0.9999) for RB5 (3)
Abs = 26.149c – 0.004 (R^2 = 0.9999) for PN H-EXL (4)

where c is the dye concentration expressed in g L^{-1}.

2.3.2. Organic matter removal measurements

The organic matter removal was calculated from COD measurements [20] as follows:

$$COD\ removal\ (\%) = \frac{(COD_i - COD_t)}{(COD_i)} \times 100 \quad (5)$$

where COD_i corresponds to the initial value and COD_t is the value at time t.

2.4. Halogenated compounds study

The formation and further removal of halogenated compounds in treated effluents were evaluated. Analyses were carried out in a Shimadzu QP 2010 (GCMS) with head space technique for the injection of the samples.

- Head space injection: 20 mL of the samples were heated to 80ºC for 45 min in a 30 mL vial sealed with silicon/PTFE septum and 1 mL of air was injected into the GCMS.

- GCMS conditions:

  - GC: - Column program T: initial 40ºC (10 min), increasing gradient rate 5ºC min^{-1}, final 225ºC (10 min)

- Injection T: 230ºC
- Carrier gas: He, flow 22.1 mL min^{-1}
- Injection mode: Split
- Split ratio: 1/20
- Column flow: 0.95 mL min^{-1}

- MS: - Ion source T: 200ºC
- Interface T: 250ºC
- Solvent cut time: 2 minutes
- Acquisition mode: SIM

Identification of the compounds was performed using Nist 147, Nist 27 and Wiley 229 as reference libraries.

In this study, 25 halogenated compounds were analyzed in each sample. A standard solution from Accustandard 0.2 mg L^{-1} was used to determine a calibration curve. Compounds and detection limits (D.L.) are listed in Table 1. As internal standard (I.S.) p-bromofluorobenzene was selected and used for the quantification of all compounds.

Table 1. Organic halogenated compounds and their detection limits.

Compound	CAS Number	D.L. (μgL^{-1})
1,1-Dichloroethene	75-35-4	2.5
Dichloromethane	75-09-2	1.0
t-1,2-Dichloroethene	156-60-5	2.5
c-1,2-Dichloroethene	156-59-2	2.5
Chloroform	67-66-3	1.0
1,1,1-Trichloroethane	71-55-6	2.5
Tetrachloromethane	56-23-5	2.5
1,2-Dichloroethane	107-06-2	10
Trichloroethene	79-01-6	1.0
1,2-Dichloropropane	78-87-5	5
Bromodichloromethane	75-27-4	5
c-1,3-Dichloropropene	10061-01-5	10
t-1,3-Dichloropropene	10061-02-6	10
1,1,2-Trichloroethane	79-00-5	10
Tetrachloroethene	127-18-4	1.0
Dibromochloromethane	124-48-1	10
Chlorobenzene	108-90-7	1.0
Bromoform	75-25-2	10
1,3-Dichlorobenzene	541-73-1	1.0
1,4-Dichlorobenzene	106-46-7	0.5
1,2-Dichlorobenzene	95-50-1	0.5
1,3,5-Trichlorobenzene	108-70-3	1.0
1,2,4-Trichlorobenzene	120-82-1	1.0
Hexachlorobutadiene	87-68-3	0.5
1,2,3-Trichlorobenzene	87-61-6	1.0

2.5. Kinetic evaluation

After the electrochemical treatment, an increase of decolourization was observed depending on NaCl concentration and UV exposure time. For this step, first-order reactions were assumed and the decolourization rate constants were calculated from the slope of the semilogarithmic plot colour (peak absorbance at λ_{max}= 488 nm for RO4) versus exposition time, in accordance with the kinetic equation:

$$\ln(Abs_t/Abs_0) = k_d \cdot t \quad (6)$$

where k_d is the first-order decolourization kinetic constant expressed in min^{-1}; Abs_t and Abs_0 are the absorbances at time t and initial respectively.

3. Results and discussion

Results are structured in two parts: sections 3.1, 3.2, 3.3 and 3.4 are focused on the study of the dye RO4. In the second part (section 3.5) RB5 and PN H-EXL were selected to verify the behaviour of other reactive dyes.

3.1. Decolourization study

Figure 2 shows the evolution of the UV-visible spectra of the dye RO4 solution (containing 0.5 g L^{-1} NaCl) during the different steps of treatment.

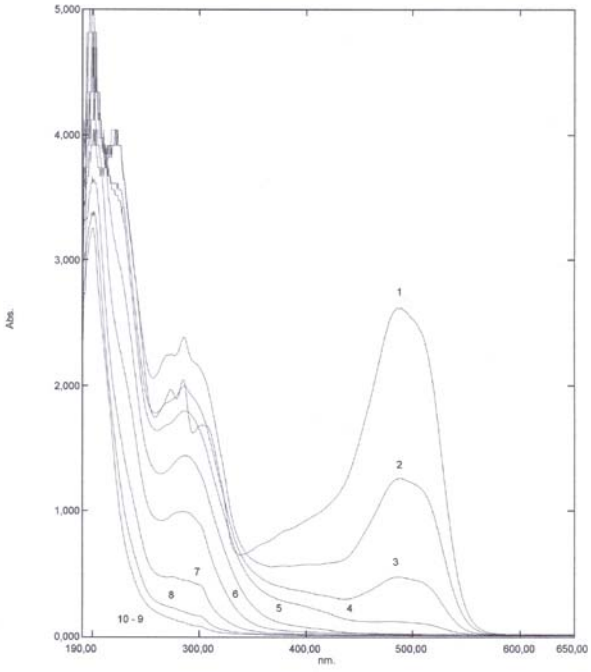


Fig. 2. Evolution of decolourization of Reactive Orange 4 (0.1 g L^{-1}) after electrochemical treatment (20 L h^{-1}, 6 mA/cm^2) and during UV light irradiation (254 nm, 6 W). Curves: (1) initial, (2) immediately after electrochemical treatment at 6 mA/cm^2, (3) 15 min UV, (4) 30 min UV, (5) 45 min UV, (6) 60 min UV, (7) 2 hours UV, (8) 3 hours UV, (9) and (10) 4 and 10 hours UV respectively (same line).

It can be seen that the absorbance in the visible region was partially reduced after the electrochemical experiment (performed at 6 mA/cm^2) and completely removed later by applying UV light.

During the UV irradiation step, the absorbance evolution in the visible spectrum region (evaluated at the dye maximum wavelength) was found to be mainly influenced by the current density applied in the electrochemical treatment and chloride ion concentration in the solution (figure 3).

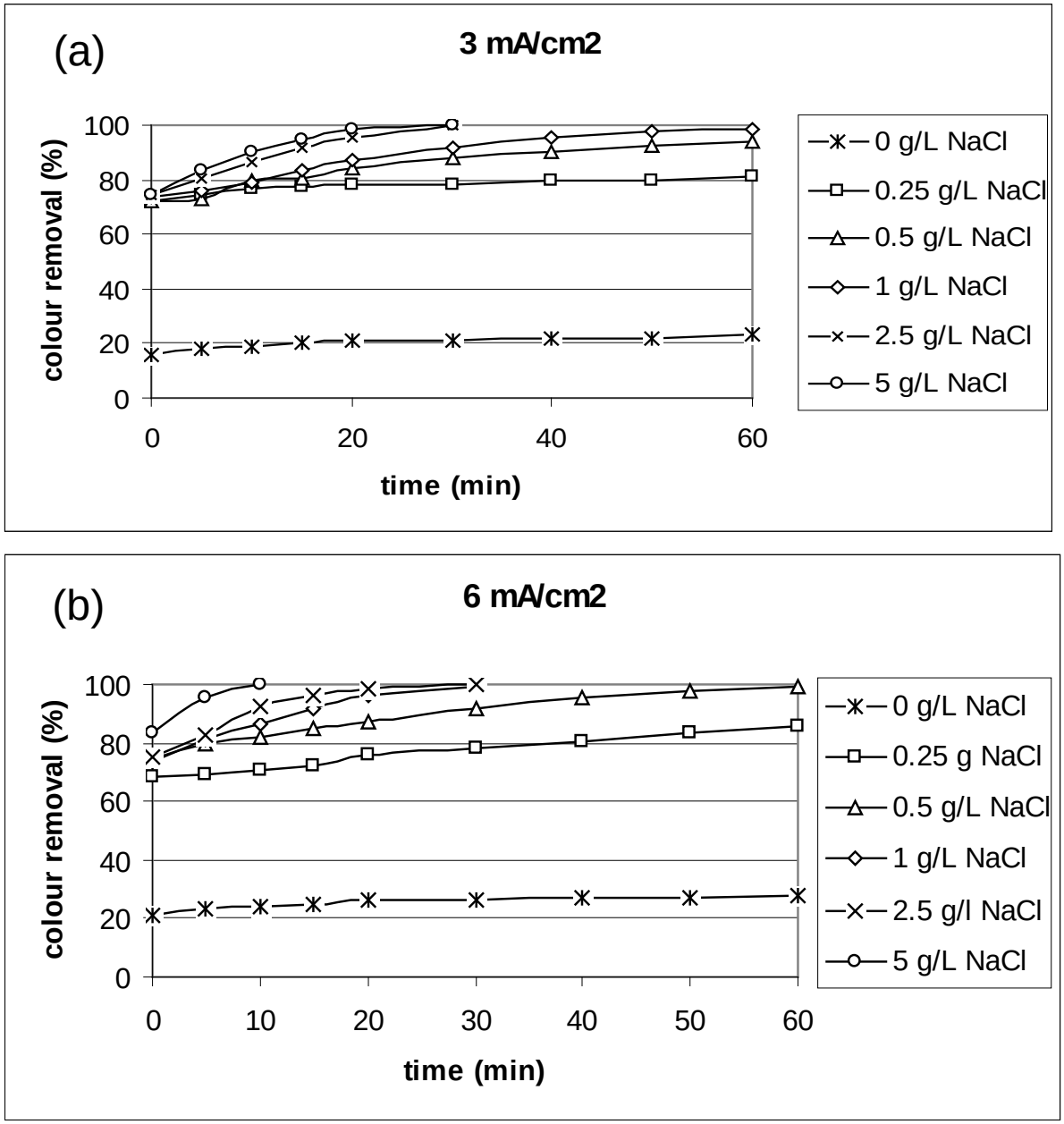


Fig. 3. Influence of different NaCl concentrations on color removal of Reactive Orange 4 (0.1 g L^{-1}) due to UV light exposure (254 nm, 6 W) after electrochemical treatment (20 L h^{-1}). Current density: a) 3 mA/cm^2 and b) 6 mA/cm^2.

The electrochemical treatment was performed at two different current densities, 3 and 6 mA/cm^2. From Figures 3.a and 3.b it can be appreciated that colour removal due to electrochemical treatment (time t = 0 min. of UV light exposure) was greater when current density was also greater.

The highest differences in the colour removal behaviour were clearly attributed to action of chloride ion. The electrochemical treatment showed poor results of decolourization and the later UV exposure was also ineffective in the absence of chlorine.

In Figure 3.a, it can be seen that more than 95% of decolourization was reached in solutions containing between 0.5 to 5 g L^{-1} NaCl after 60 minutes of UV light exposure. Even when using only 0.25 g L^{-1} of NaCl an 80% of colour removal was reached for the same exposure time.

In figure 3.b, values of colour removal were higher than in figure 3.a, as the current density was also higher but a similar general behaviour was observed. Again 0.25 g L^{-1} of NaCl provided slightly lower colour removal results: 85% of colour removal after 60 minutes of UV exposure. In this experiment, all other NaCl concentrations reached at least 98% of colour removal before 60 min of UV exposition.

Textile wastewater contains large quantities of inorganic salts, usually $NaSO_4$ or NaCl used as dyeing electrolyte. These salts increase the conductivity of the effluent [21, 22], which improves the efficiency of the electrochemical reaction. The case where the only electrolyte used in the effluent was Na_2SO_4 (that is 0 g L^{-1} NaCl) is very unlike in dyehouse effluents, as usually dyeing is carried out with decalcified tap water which always contains a certain amount of chloride. A NaCl concentration between 0.25 and 0.5 g L^{-1} corresponds to a Cl^- concentration in water between 153 and 306 ppm. In the case of Barcelona area, the main line tap water contains about 200 ppm Cl^- (approximately 0.3 g L^{-1} NaCl). This implies that when $NaSO_4$ is used as dyeing electrolyte, the Cl^- present in the main line tap water is enough to provide a high decolourization level without the further addition of NaCl to carry out the treatment.

From the experimental results performed on dye solutions containing NaCl between 0.25 and 0.5 g L^{-1}, it can be concluded that after an electrochemical treatment at 3 mA/cm^2 and a later UV radiation treatment during 60 minutes, at least an 80% of colour removal is achieved. This discolouration of the effluent is sufficient and treatments more intensive are not required. We must consider that the contribution of the coloured effluents to the total plant wastewater is only about a 10%. The dilution with the rest of process effluents and the subsequent biological treatment ensure that final wastewater will be able to accomplish regulations.

3.2. Decolourization kinetic constants (K_d)

In the dye decolourization process, the breakage of azo bound (-N=N-) leads to the elimination of colour [23].

The decolourization catalysed by UV light follows a pseudo-first order reaction, in other words, a first-order law with respect to dye concentration. Decolourization kinetic constants (k_d) were calculated at different NaCl concentrations and current densities, in order to

determine the optimal conditions for electrochemical treatment-UV exposure colour removal (table 2).

Table 2. Decolorization kinetics constants (k_d) of Reactive Orange 4.

K_d (min^{-1})												
Current density (mA/cm^2)	NaCl conc. (g/L)											
	0		0.25		0.5		1		2.5		5	
	k_d	R^2	k_d	R^2	k_d	R^2	k_d	R^2	k_d	R^2	k_d	R^2
3	0.0012	0.99	0.0051	0.98	0.0261	0.98	0.0469	0.99	0.867	0.99	0.1404	0.99
6	0.0031	0.99	0.0136	0.99	0.0558	0.99	0.0927	0.98	0.2089	0.98	0.4256	0.99

From k_d results it is possible to state that decolourization kinetic constants values depend on the NaCl concentration as well as current density: decolourization is greater when applying higher current densities and greater NaCl concentration.

When Na_2SO_4 is used as only electrolyte (NaCl concentration 0 g L^{-1}) decolourization constants values are very low and consequently, colour removal in the effluent is very slow.

In general, for each current density, k_d values double when NaCl concentration is increased two times, except for 0.25 and 0.5 g L^{-1} where the relationship between constants values are five. This fact permit to confirm this NaCl concentration as the minimum required to use electrochemical treatment followed by UV exposure as a colour removal method.

3.3. Influence of the UV light in organic matter removal

Organic matter removal of the effluent due to electrochemical treatment and UV exposure was evaluated by COD measurements [24, 25].

At the lower current density (3 mA/cm^2) and immediately after electrochemical treatment, the COD decreased an 11% and it reached a 15% after 60 minutes of UV irradiation. When current density applied was 6 mA/cm2, the COD removal was a 17% in the first step and a 20% in the combined process after 60 minutes of UV treatment. The maximum organic matter removal accomplished was a 38%. It was reached at 6 mA/cm^2, after four hours of UV light exposure (COD values are listed in section 3.5).

A full mineralization could be reached with a higher intensity electrochemical treatment [26, 27] and probably also with a more intense UV exposition (or a combination of both) but economical cost of the process would be very high what makes it a non attractive method to be applied at industrial scale for the mineralization of dyeing effluents. Complete degradation of textile effluents can be achieved by several other methods, such as conventional activated sludge biological treatments, at lower economical costs.

For this reason, the combination of electrochemical techniques with UV treatment is proposed as a previous step to the biological treatment, where the coloured effluents (about the 10% of the total plant effluents) are treated separately and, once the dyes molecules have been broken and converted in smaller size and more biodegradable compounds, they can be easily treated in the biological plant with the rest of effluents (scouring, bleaching, washing, etc.). The colour removal by electrochemical treatment-UV irradiation after the biological treatment is also possible, although it is less in advantageous as a much higher volume of water must be treated.

More details about dye degradation when applying UV light can be obtained from figure 2 where the evolution of the effluent absorbance during its exposition to UV light versus time is shown. There are three important regions to be studied. The first one is centred at 488 nm and shows how the effluent is decolourized, mainly attributed to the azo bounds breakages. The second area is the band at λ_{max} 290 nm which corresponds to the aromatic rings of the dye. The intensity of this band decreases in time during UV exposure, due to the degradation of the aromatic dye fragments. Finally, the third region, absorption under 200 nm, can be attributed to carboxylic acid accumulated at the final stage of the oxidation. This represents the residual COD present in the effluent [28].

The evolution of these three bands shows clearly that the combination of electrochemical and UV light exposure produces a breakage of the molecular bonds of the dye. Although the mineralization obtained is not too high under these experimental conditions, it is predictable that the production of simpler molecules would facilitate the further mineralization by biological methods.

3.4. Influence of the UV light in organic halogenated compounds

Although the use of electrochemical treatment to decolourize effluents has been recognized as a very effective technique, the main disadvantage of the method is the formation of small amounts of organic halogenated compounds when chloride ion is the solution [29]. But the evolution on these compounds when subsequent UV irradiation is applied to the effluent has not still been reported. For this reason, an extensive study about the formation of volatile organic halogenated compounds was performed by GCMS. Figure 4 shows a typical chromatogram obtained.

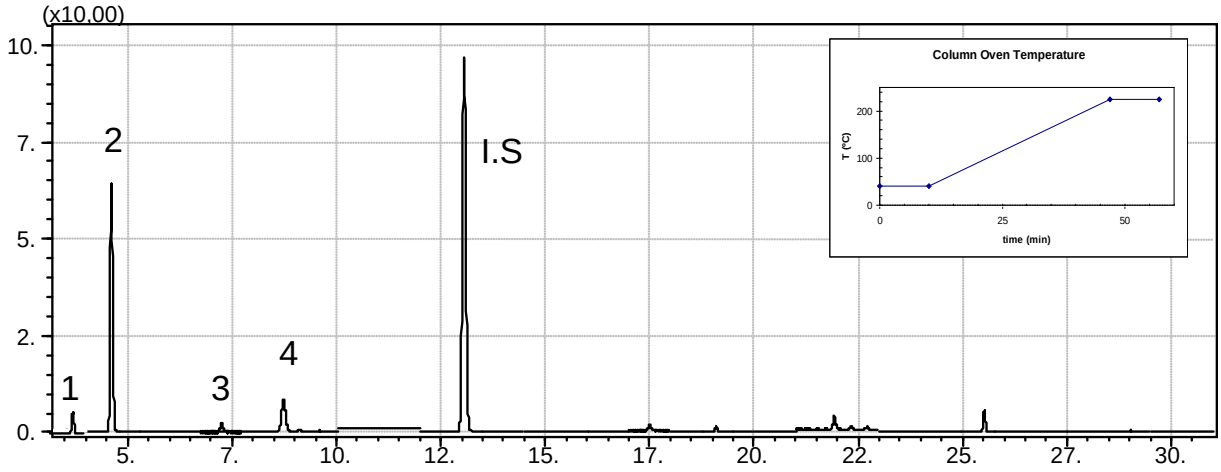


Fig. 4. Chromatogram of Reactive Orange 4 treated at 3 mA/cm^2 and containing 0.5 g L^{-1} of NaCl. [1] Dichloromethane, [2] Chloroform, [3] Trichloroethylene and [4] Bromodichloromethane. I.S. is the Internal Stanrdard, p-Bromofluorobenzene.

The compounds formed are dichloromethane, chloroform, trichloroethylene, bromodichloromethane mainly at ppb concentrations, as indicated in Figure 4 and in Table 3. The formation of bromodichloromethane is attributed to the bromide trace impurities of the NaCl.

Table 3. Concentrations (mg/L) of halogenated compounds generated during the treatment of Reactive Orange 4, current density 3 mA/ cm^2 at different NaCl concentration.

NaCl Conc. (g/ L)	Treatment	Dichloromethane (ppm)	Chloroform (ppm)	Trichloroethylene (ppm)	Bromodichloromethane (ppm)
0	After electrochemical	0.001	0.06	0.002	< D.L.
0.5	Initial (before electrochemical)	< D.L.	0.02	0.003	< D.L.
	After electrochemical	0.004	0.27	0.004	0.002
	After 60 min. of UV exposure	0.004	0.11	0.003	< D.L.
10	After electrochemical	0.006	2.83	0.02	0.06

This table shows the organic halogenated compounds evolution along the combined treatment and the influence of NaCl concentration in the effluent in the formation of these compounds.

From the results in Table 3, it can be concluded that the greater the NaCl concentration is, the greater the organic halogenated compounds generation is. Because of this fact, when an electrochemical treatment should be performed to the effluent, Na_2SO_4 must be selected as the only dyeing electrolyte in order to minimize the organic halogenated compounds formation. An important result of section 3.1 is that in the case of dyeing effluents, the small Cl^- concentration present in the decalcified main line tap water is enough to reach a good decolourization level. Consequently, no additional NaCl is required to obtain of good decolourisation of the residual dyebaths.

Current density applied during the electrochemical treatment is also an important factor in organic halogenated compounds generation. Low current densities produce less organic halogenated compounds. Chloroform is the compound formed in greater extension. After electrochemical treatment, the concentration of this compound is quite higher than initially, but UV exposure achieves a significant reduction of its concentration. It is possible to state that UV exposure of the effluent after the electrochemical treatment removes up to a 75% of organic halogenated compounds generated during the electrochemical treatment.

3.5. Other dyes

In this section, two other reactive dyes, RB5 and PN H-EXL, were studied to evaluate their behaviour versus RO4. For this purpose, studies of decolourization, organic matter removal and organic halogenated compounds were performed.

Figure 5 shows the decolourization of dye effluents containing 0.5 g L^{-1} NaCl after applying an electrochemical treatment at 6 mA/cm^2 followed by UV light irradiation.

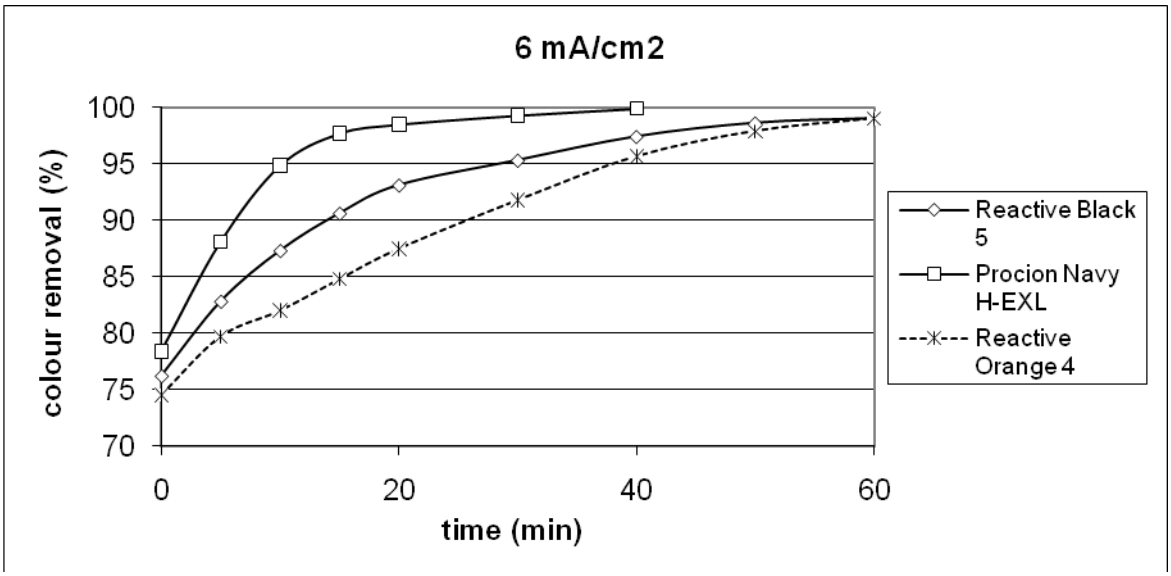


Fig. 5. Evolution of color removal for Reactive Orange 4, Reactive Black 5 and Procion Navy H-EXL after electrochemical treatment (6 mA/cm^2) plus UV light irradiation of effluents containing 0.5 g L^{-1} NaCl.

Comparing the evolution of the three dyes, it is possible to state that RB5 and PN H-EXL effluents can be treated in the same way that RO4 to remove colour, as their decolourization is even faster for the same conditions.

With respect to the influence of the UV light degradation on the organic matter removal, the three dyes showed a similar degradation, being even more alike in the case of RO4 and RB5 (table 4). After electrochemical treatment at 6 mA/cm^2, RO4 degradation was a 17%, reaching a 25% after 60 minutes of UV light exposure. For RB5 results were 15% and 29% respectively; whereas 18 and 28% were obtained for PN H-EXL, respectively (table 4).

Table 4. COD values ($mO_2\ L^{-1}$) and COD removal (%) for Reactive Orange 4, Reactive Black 5 and Procion Navy H-EXL after electrochemical treatment (3 mA/cm^2 and 6 mA/cm^2) and after 60 and 240 min. of UV light exposure (254 nm, 6 W).

Dye, Current density	COD values (mg $O_2\ L^{-1}$)				COD removal (%)		
	Initial	After electroch.	UV 60 min.	UV 240 min.	After electroch.	UV 60 min.	UV 240 min.
RO4, 3 mA/cm^2	59	52	50	43	11	15	27
RO4, 6 mA/cm^2	59	49	44	36	17	25	38
RB5, 6 mA/cm^2	154	131	109	97	15	29	37
PNH-EXL, 6 mA/cm^2	39	32	28	24	18	28	35

Finally, the influence of the UV light in organic halogenated compounds degradation for RB5 and PN H-EXL is reported in Table 5. The same compounds that in the case RO4 were identified.

Table 5. Concentrations (mg L^{-1}) of organic halogenated compounds for Reactive Black 5 and Procion Navy H-EXL (current density 6 mA/cm^2 and 0.5 g L^{-1} NaCl).

Dye	Treatment	Dichloromethane (ppm)	Chloroform (ppm)	Trichloroethylene (ppm)	Bromodichloromethane (ppm)
Reactive Black 5	Before Electrochemical	0.001	0.003	0.002	< D.L.
	After Electrochemical	0.002	0.49	0.002	0.001
	After 60 min. of UV exposure	0.002	0.17	0.001	< D.L.
Procion Navy H-EXL	Before Electrochemical	0.0045	< D.L.	0.004	< D.L.
	After Electrochemical	0.0065	0.49	0.005	0.004
	After 60 min. of UV exposure	0.0049	0.13	0.004	0.001

The quantitative results showed again a similar behaviour that RO4. Electrochemical process increased the concentrations of these compounds, especially chloroform, and UV light exposure removed them in a great extent.

4. Conclusions

The application of UV light irradiation after electrochemical treatment improves the yield of the first process in the degradation of reactive dyes in terms of colour removal and organic matter removal. The combination of the two techniques allows to perform the electrochemical treatment at lower current densities.

A small amount of Cl^- ion is recommended in order to obtain an effective combination of electrochemical treatment and UV exposure, the optimum was found to be between 0.25 and 0.5 g/L NaCl. In this range, decolourization kinetic constants values (k_d) are much greater than expected and a 95% of colour removal can be reached in short exposition times.
During the electrochemical treatment, some halogenated compounds can be formed due to the chloride reactions. When working at low current densities, as the selected in this study, only four halogenated compounds were detected after the electrochemical treatment, being the chloroform the only one significant. Their concentrations were dramatically reduced when the NaCl concentration decreased. In addition, the UV irradiation showed a chloroform destruction up to a 75%.

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553 REFERENCES
554
555 [1] M. Zhou, J. He, Degradation of cationic red X-GRL by electrochemical oxidation on
556 modified PbO_2 electrode, J. Hazard. Mater. 153 (2007) 357-363.
557
558 [2] R. Pelegrini, P. Peralta-Zamora, R. de Andrade, A. Reyes, J. Durán, Electrochemical
559 assisted photocatalytic degradation of reactive dyes, App. Cat. B: Environ. 22 (1999)
560 83-90.
561
562 [3] S. R. Camp, P. E. Strurrock, The identification of the derivates of C.I. Reactive Blue 19
563 in textile wastewater, Water Res. 24 (1990) 1275-1278.
564
565 [4] Skoog, D. A., Holler, F. J., Nieman, T. A., Principios de análisis instrumental, fifth ed.,
566 McGraw-Hill, Madrid, 2001.
567 [5] M. N. Priya, K. Palanivelu, Electrochemical treatment of a reactive dye effluent using
568 solar energy, Color. Technology 121 (2005) 198-202.
569
570 [6] H-Y, Shu, M-C, Chang, Decolourization effects of six azo dyes by O_3, UV/O_3 and
571 UV/H_2O_2 processes, Dyes Pigments 65 (2005) 25-31.
572
573 [7] V. López-Grimau, M.C. Gutiérrez, Decolorisation of simulated reactive dyebath
574 effluents by electrochemical oxidation assisted by UV light, Chemosphere 62 (2006)
575 106-112.
576
577 [8] D. Rajkumar, B. J. Song, J. G. Kim, Electrochemical degradation of Reactive Blue 19 in
578 chloride medium for the treatment of textile dyeing wastewater with identification of
579 intermediate compounds, Dyes Pigments 72 (2007) 1-7.
580
581 [9] J. Swamy, J. Ramsay, The evaluation of white rot fungi in the decoloration of textile
582 dyes, Enzyme Microb. Technol. 24 (1999) 130-137.
583
584 [10] M.C. Gutiérrez, Contribución al estudio de la decoloración electroquímica de colorantes
585 reactivos en aguas residuals textiles, thesis dissertation, UB and UPC, Barcelona, 2000,
586 pp. 255.
587
588 [11] A. Marcinek, R. Podsiadly, J. Sokolowska, J. Zielonka, A. Socha, M. Kazmierska, The
589 relationship between the electrochemical and photochemical reduction of some azo dyes
590 derived from 2-aminobenzothiazole, J. Photochem. Photobiol. A: Chem. 171 (2005) 69-
591 76.
592
593 [12] L. Szpyrkowicz, C. Juzzolino, S. Kaul, A comparative study on oxidation of disperse
594 dyes by electrochemical process, ozone, hypochlorite and fenton reagent, Water Res. 35
595 (2001) 2129-2136.
596
597 [13] J. Albertí, G. Sánchez, Proceso EKAR: aplicación de tecnologías electroquímicas al
598 tratamiento de aguas residuales industrials, Tecnol. Agua 205 (2000) 61-68.
599

[14] M. Zanoni, P. Carneiro, M. Osugi, C. Fugivara, N. Boralle, M. Furlan, Evaluation of different electrochemical methods on the oxidation and degradation of Reactive Blue 4 in aqueous solution, Chemosphere 59 (2004) 431-439.

[15] B. Boye, M. M. Dieng, E. Brillas, Electrochemical degradation of 2,4,5-triclorophenoxyacetic acid in aqueous medium by peroxi-coagulation. Effect of pH and UV light, Electrochim. Acta 48 (2003) 781-790.

[16] A. G. Vlyssides, M. Loizidou, P. K. Karlis, A. A. Zorpas, D. Papaioannou, Electrochemical oxidation of a textile dye wastewater using a Pt/Ti electrode, J. Hazard. Mater. B70 (1999) 41-52.

[17] M. Muruganandham, M. Swaminathan, Photocatalytic decolourisation and degradation of Reactive Orange 4 by TiO_2-UV process, Dyes pigments 68 (2006) 133-142.

[18] R. Jain, S. Varshney, S. Sikarwar,Electrochemical techniques for the removal of Reactofix Golden Yellow 3 RFN from industrial wastes, J. Colloid Interface Science 313 (2007) 248-253.

[19] M. Muruganandham, M. Swaminathan, TiO_2-UV photocatalytic oxidation of Reactive Yellow 14: Effect of operational parameters, J. Hazard. Mater. 135 (2006) 78-86.

[20] A. D. Eaton, L. S. Clesceri, A. E. Greenberg, Standard Methods for the examination of water and wastewater, 19th ed., APHA AWWA WEF, Washington, 2005.

[21] G. Malpass, D. Miwa, S. Machado, A. Motheo, Decolourisation of real textile waste using electrochemical techniques: Efect of electrode composition, J. Hazard. Mater. 156 (2008) 170-177.

[22] V. López-Grimau, Decoloració electroquímica i reutilització d'efluents de tintura amb colorants reactius, thesis dissertation, UPC, Terrassa, 2007, pp. 61.

[23] M.C. Gutierrez, M. Crespi, A review of electrochemical treatments for colour elimination, J. Soc. Dyers Col. (1999) 115-342.

[24] M. Gonçalves, E. Pinto, P. Nkeonye, A. Oliveira-Campos, Degradation of C.I. Reactive Orange 4 and its simulated dyebath wastewater by heterogeneous photocatalysis, Dyes Pigments 64 (2005) 135- 139.

[25] M. Neelavannan, C. Basha, Electrochemical-assisted photocatalytic degradation of textile washwater, Separat. Purificat. Tech. 61 (2007) 168-174.

[26] L. Jin, J. Chen, M. Liu, L. Zhang, J. Zhang, Application of nano TiO2 towards polluted water treatment combined with electro-photochemical method, Water Res. 37 (2003) 3815-3820.

[27] A. Motheo, M. Catanho, G. Malpass, Photoelectrochemical treatment of the dye reactive red 198 using DSA electrodes, App. Cat. B: Environ. 62 (2006) 193-200.

[28] M. Panizza, G. Cerisola, Removal of colour and COD from wastewater containing acid blue 22 by electrochemical oxidation, J. Hazard. Mater. 153 (2008) 83-88.

[29] J.G. Kim, D. Rajkumar, Oxidation of various reactive dyes with in situ electro-generated active chlorine for textile dyeing industry wastewater-treatment, J. Hazard. Mater. B 136 (2006) 203-212.